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EXCITED STATE KINETICS OF MERCURY HALIDES AND MIXTURES
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CHEMISTRY D W SETSER 28 NOV 83 N00014-80-C-0346

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Experimental kinetic measurements were made for mercury and mercury halide systems that have relevance for mercury halide lasers operating on the B-X transitions. The quenching of Hg(³ P ₂) atoms by halogens, the vibrational relaxation of HgCl(B) and HgBr(B), and the dissociative excitation transfer from N ₂ (A) and Xe(³ P _{2,1}) to HgCl ₂ , HgBr ₂ , CH ₃ HgCl, CH ₃ HgBr and CH ₃ HgI were studied. In addition, relaxation processes in the triplet states of N ₂ were investigated; the very facile coupling between the N ₂ (W) and N ₂ (B) states was discovered and studied at the state-to-state level.		

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FINAL REPORT

EXCITED STATE KINETICS OF MERCURY HALIDES AND MIXTURES WITH N_2 AND Xe.

Contract No.
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Summary

Experimental kinetic measurements were made for mercury and mercury halide systems that have relevance for mercury halide lasers operating on the B-X transitions. The quenching of $Hg(^3P_2)$ atoms by halogens, the vibrational relaxation of $HgCl(B)$ and $HgBr(B)$, and the dissociative excitation transfer from $N_2(A)$ and $Xe(^3P_{2,1})$ to $HgCl_2$, $HgBr_2$, CH_3HgCl , CH_3HgBr and CH_3HgI were studied. In addition, relaxation processes in the triplet states of N_2 were investigated; the very facile coupling between the $N_2(W)$ and $N_2(B)$ states was discovered and studied at the state-to-state level. The coupling to $N_2(B')$ also is important for some $N_2(B)$ vibrational levels. Perhaps the most interesting feature discovered from the $Hg(^3P_2)$ atom studies was the very high branching fraction for formation of excited state mercury halides in reaction with molecular halogens, which is in strong contrast with the reactions of the lower $Hg(^3P_1)$ and $Hg(^3P_0)$ states. Since our work either has been published or is in manuscript form, this final report is presented in the form of a listing of abstracts of papers that have been or soon will be published. The listing is given in three categories.

- I) Excited state kinetics of $N_2(A)$, $N_2(B)$ and excitation-transfer reactions to Mercury (II) halides.
- II) Quenching and excitation transfer reactions of metastable rare gas atoms with HgX_2 and Hg.
- III) State-to-state kinetics for quenching of $Hg(^3P_2)$ atoms by halogen containing molecules and vibrational relaxation of $HgCl(B)$ and $HgBr(B)$.

I. Excited State Kinetics of $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$ and Excitation Transfer

Reactions to HgX_2 Molecules.

1) PRODUCTION OF THE N_2 HERMAN INFRARED SYSTEM BY THE ENERGY POOLING REACTION OF $N_2(A^3\Sigma_u^+)$ METASTABLE NITROGEN MOLECULES

I. Nadler, D. W. Setser and S. Rosenwaks, Chem. Phys. Lett., 72, 536 (1980).

Molecular N_2 emission, observed from an $Ar(^3P_{0,2})$ and $Xe(^3P_2) + N_2$ flowing afterglow apparatus, indicates that the energy pooling reaction by $2N_2(A^3\Sigma_u^+)$ generates the emission from the Herman infrared system, which is an unassigned nitrogen band system. A lower limit to the formation rate constant for the upper state of the Herman infrared system was found to be $2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The information presented here may help in the identification of the upper and lower states of the emission system. The $2N_2(A)$ energy pooling reaction also forms $N_2(B^3\Pi_g, \nu > 8)$ but a rate constant cannot be assigned from the present data.

2) ENERGY TRANSFER REACTIONS OF $N_2(A^3\Sigma_u^+)$. 5. QUENCHING BY HYDROGEN HALIDES, METHYL HALIDES, AND OTHER MOLECULES

W. G. Clark and D. W. Setser, J. Phys. Chem., 84, 2225 (1980)

The 300 K quenching rate constants for $N_2(A^3\Sigma_u^+, \nu' = 0, 1)$ have been measured with 20 small molecules, mostly of the hydrogen halide or methyl halide variety. The metastable $N_2(A)$ molecules were prepared by the reaction of $Ar(^3P_{0,2})$ with N_2 in a discharge-flow system. Rate constants were measured by observing the variation of the $N_2(A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+)$ emission intensity as a function of added reactant concentration. The magnitude of the rate constants increase in the HX and CH_3X series as X changes from F to I . The temperature dependence of the NO , O_2 , C_2H_2 , and C_2H_4 reactions were qualitatively investigated with the discharge flow technique by comparing experiments at ~ 120 and 300 K. On the basis of the limited data, the rate constants are either virtually invariant with temperature or decrease mildly with decreasing temperature. In contrast the $N_2(A)$ bimolecular, energy pooling, $N_2(C)$ formation rate constant appears to increase with decreasing temperature. The results of the present study are compared to previous investigations from this laboratory and to other studies of $N_2(A^3\Sigma_u^+)$.

3) QUENCHING OF $N_2(A^3\Sigma_u^+)$ BY $Hg(II)$ HALIDES

T. D. Dreiling and D. W. Setser, Chem. Phys. Lett., 74, 211 (1980)

The flowing afterglow technique has been used to study the reactions of $N_2(A^3\Sigma_u^+, \nu = 0, 1)$ with some methylmercury and mercuric halides. Room temperature quenching rate constants and rate constants for production of $HgX(B^2\Sigma^+)$ were measured. Evidence is presented that shows another electronic state of N_2 , besides $N_2(A)$, can produce $HgX(B)$ via dissociative excitation reactions with HgX_2 .

4) COLLISIONAL COUPLING OF $N_2(B^3\Pi_g)$ AND $N_2(W^3\Delta_u)$ STATES: STUDIED BY LASER-INDUCED FLUORESCENCE

N. Sadeghi and D. W. Setser, Chem. Phys. Lett., 77, 304 (1981)

The $N_2(B^3\Pi_g)$ state was produced by laser excitation of $N_2(A^3\Sigma_u^+)$ in Ne or Ar carrier gas in a flowing afterglow apparatus. All of the vibrational levels initially populated by the laser, $v' = 3-10$, showed double exponential relaxation. The initial fast decay is associated with collisional coupling of the $N_2(B, v')$ level to adjacent $N_2(W^3\Delta_u)$ vibrational levels. The slow decay represents the overall decay of these coupled levels, which generates lower vibrational levels of $N_2(B^3\Pi_g)$.

5) PRIMARY $N_2(B)$ VIBRATIONAL DISTRIBUTIONS FROM EXCITATION-TRANSFER REACTIONS BETWEEN $Kr(^3P_2)$ OR $Xe(^3P_2)$ ATOMS AND N_2

N. Sadeghi and D. W. Setser, Chem. Phys. Lett., 82, 44 (1981)

Low-pressure flowing afterglow experiments with Ne carrier gas have been performed to obtain the initial $N_2(B)$ vibrational distributions and the $N_2(B)$ formation rate constants for $Xe(^3P_2)$ and $Kr(^3P_2)$ excitation-transfer reactions to N_2 . The $N_2(C)$ formation rate constant for $Ar(^3P_2) + N_2$ also was measured. The results are consistent with a very specific interaction mechanism favoring only a few of the many available N_2^* exit channels.

6) COLLISIONAL COUPLING AND RELAXATION OF $N_2(B^3\Pi_g)$ AND $N_2(W^3\Delta_u)$ VIBRATIONAL LEVELS IN Ar AND Ne

N. Sadeghi and D. W. Setser, J. Chem. Phys., 79, 2710 (1983)

Laser excitation from $N_2(A^3\Sigma_u^+, v=0-6)$ in Ne and Ar carrier gas in a flowing afterglow apparatus has been used to prepare $N_2(B^3\Pi_g)$ molecules in individual levels from $v'=3-10$. The subsequent $N_2(B-A)$ fluorescence intensity was observed to study the coupling and relaxation kinetics of $N_2(B^3\Pi_g, v=2-10)$. The decay curves from each level show double (or higher) exponential relaxation. The first component is assigned as primarily the rapid coupling of the $N_2(B^3\Pi_g, v)$ and $N_2(W^3\Delta_u, v$ or $v+1)$ levels, however, the $N_2(B^3\Sigma_u^-, v-4)$ levels also may be involved for $N_2(B, v \geq 5)$. The slowest decay component represents the subsequent relaxation of the coupled levels. The combination of the two steps is equivalent to apparent stepwise vibrational relaxation of $N_2(B^3\Pi_g, v)$; such relaxation occurs even at low Ar pressure because of the large rate constants and long radiative lifetimes of $N_2(B)$ and $N_2(W)$. The coupling pattern between $N_2(B)$ and $N_2(W)$ is analyzed, and rate constants are assigned to elementary steps in the relaxation sequence and the scheme is evaluated. From the analysis of the slow decay components in argon, estimates (20-90 μs) are obtained for the radiative lifetimes for the reservoir levels, which are assigned as $N_2(W^3\Delta_u, v)$ for $N_2(B, v < 4)$ and $N_2(W^3\Delta_u, v$ or $v+1)$ levels and possibly $N_2(B^3\Sigma_u^-, v-4)$ levels for $N_2(B, v \geq 5)$.

II. Quenching and Excitation-Transfer Reactions of Metastable Rare Gas Atoms with Hg and HgX₂.

1) DISSOCIATIVE EXCITATION OF Hg(II) HALIDES BY Xe(³P₂) AND Xe(³P₁)

T. D. Dreiling, D. W. Setser and S. Ferrero, J. Chem. Soc. Faraday Transactions 2, 78, 1311 (1982)

Rate constants for the production of excited state products from the reaction of Xe(³P₂) with several methylmercury and mercuric halides have been measured in a flowing afterglow at elevated temperatures. The most important product is HgX(B³Σ⁺), X = Cl, Br, I for all reagents studied. Minor amount of HgX(D & ³C²Π) and XeX(B) emission also were observed. Sensitization experiments with Xe(³P₁) and HgCl₂ gave the same result. For HgCl₂ and HgBr₂, the HgX(B) formation rate constants are large (~10⁻⁹ cm molec⁻¹ sec⁻¹), which suggests that quenching of Xe gives HgX* with a branching ratio of nearly unity. The HgX(B) formation rate constants from CH₃HgX compounds are about an order of magnitude smaller than for the HgX₂ compounds. Reactions of both CH₃HgX and HgX₂ compounds with He(2³S), Ne(³P₂), Ar(³P₂), and Kr(³P₂) gave predominantly Hg emission.

2) QUENCHING RATE CONSTANTS OF METASTABLE ATOMS OF NEON, ARGON, AND KRYPTON BY MERCURY ATOMS

D. J. Wren and D. W. Setser, J. Chem. Phys. 74(4), 2331 (1981)

Room temperature rate constants (thermal average cross-sections) for the quenching of electronically excited state rare gas metastable atoms by mercury atoms have been measured using the flowing afterglow technique. The thermal cross sections are σ₀[Ne(³P₂)] = 70 Å²; σ₀[Ar(³P₂)] = 194 Å; σ₀[Ar(³P₀)] = 219 Å²; and σ₀[Kr(³P₂)] = 124 Å². The mechanism for quenching by mercury atoms is Penning ionization for Ne* and Ar* and excitation transfer for Kr*. These results are discussed in terms of the cross-section of similar reagents and the cross-section predictions of the close collision criteria. The large experimental cross-sections indicate that the total quenching cross-section is dictated by interactions occurring at large internuclear distances associated with a long range attractive potential. However, the interactions at shorter range are responsible for the actual conversion from reactants to products. The Kr(³P₂) + Hg excitation transfer reaction provides a way to generate Hg(³P₂) metastable atoms in a flowing afterglow apparatus.



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III. State-to-State Kinetics for Quenching of $\text{Hg}(^3\text{P}_2)$ Atoms by Halogen Containing Molecules and Vibrational Relaxation of $\text{HgCl}(\text{B})$ and $\text{HgBr}(\text{B})$.

- 1) A FLOWING AFTERGLOW SOURCE OF $\text{Hg}(^3\text{P}_0)$ and $\text{Hg}(^3\text{P}_2)$: APPLICATION TO $\text{HgX}(\text{B})$, $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ FORMATION KINETICS

T. D. Dreiling and D. W. Setser, J. Phys. Chem. 86, 2276 (1982)

Passing a mercury saturated flow of Ar through a low power, hollow-cathode discharge gives $\text{Hg}(^3\text{P}_2)$ and $\text{Hg}(^3\text{P}_0)$ metastable atom concentration of $\sim 5 \times 10^9$ atoms cm^{-3} in a flowing afterglow reactor. The reaction of $\text{Hg}(^3\text{P}_2)$ with halogens have been studied by observation of the low pressure, collision-free $\text{HgX}(\text{B})$, $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I chemiluminescence. This appears to be the first report of the $\text{Hg}(\text{B-X})$ emission spectrum.

- 2) INTERPRETATIONS OF THE MERCURY HALIDE ($\text{B}^2\Sigma^+ - \text{X}^2\Sigma$) CHEMILUMINESCENCE FROM REACTIVE QUENCHING OF $\text{Hg}(^3\text{P}_2)$ BY HALOGEN CONTAINING MOLECULES

T. D. Dreiling and D. W. Setser, J. Chem. Phys. 79, Dec. (1983)

The $\text{HgX}(\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+)$, $\text{X} = \text{halogen}$, emission spectra have been recorded from $\text{Hg}(^3\text{P}_2)$ atom reaction with several halogen containing molecules using a flowing afterglow reactor. The HgX^* emission intensities were compared with the HgCl^* emission intensity from $\text{Hg}(^3\text{P}_2) + \text{Cl}_2$ to assign rate constants for $\text{HgX}(\text{B})$ formation. The $\text{Hg}(^3\text{P}_2) + \text{diatomic halogen}$ reactions have large k_{HgX^*} and their branching fractions for $\text{HgX}(\text{B})$ formation are probably unity. The polyatomic reagents generally gave much smaller k_{HgX^*} ; although, a few moderately good donors, e.g., CF_3I , CBr_4 , CCl_4 and NF_3 were identified. The experimental spectra were numerically simulated to assign $\text{HgX}(\text{B})$ vibrational energy distributions. A decrease in $\langle f_v(\text{HgX}) \rangle$ was found for the Cl_2 , Br_2 , I_2 series which is analogous to previous findings for $\langle f_v(\text{XeX}) \rangle$ from reactive quenching of $\text{Xe}(^3\text{P}_2)$. Possible reasons for the similarity are discussed. The $\text{HgX}(\text{B})$ vibrational energy disposal for polyatomic reagents is compared to analogous data for reaction of alkaline earth metal atoms and $\text{Xe}(^3\text{P}_2)$.

- 3) MERCURY HALIDE $\text{B}(^2\Sigma^+)$ VIBRATIONAL DISTRIBUTIONS FROM DISSOCIATIVE EXCITATION REACTIONS OF Hg HALIDES WITH $\text{Xe}(^3\text{P}_2)$ AND $\text{N}_2(\text{A}, ^3\Sigma_u^+)$

T. D. Dreiling and D. W. Setser, J. Chem. Phys., 79, Dec. (1983)

The $\text{HgX}(\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+)$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$, spectra from the dissociative excitation reactions of $\text{N}_2(\text{A}, ^3\Sigma_u^+)$, $v = 0, 1$ and $\text{Xe}(^3\text{P}_2)$ with several mercuric and methylmercury halides have been simulated to assign the $\text{HgX}(\text{B})$ vibrational distributions. The distributions from the methylmercury halides could be described as Boltzmann types with temperatures ranging from 1000K for $\text{N}_2(\text{A}) + \text{CH}_3\text{HgI}$ to 9000K for $\text{Xe}(^3\text{P}_2) + \text{CH}_3\text{HgCl}$. The distributions from the mercuric halides are non-Boltzmann and the $\langle f_v \rangle$ are somewhat higher than for the CH_3HgX compounds. The initial $\text{HgX}(\text{B})$ vibrational distributions are used to discuss the state-to-state quenching mechanisms.

4) A FLOWING AFTERGLOW STUDY OF THE QUENCHING REACTIONS OF $\text{Hg}(^3\text{P}_2)$ AND $\text{Hg}(^3\text{P}_0)$ ATOMS BY HALOGENS, MIXED HALOGENS AND POLYATOMIC HALIDES

Fu Min Zhang, D. Oba and D. W. Setser, J. Phys. Chem., to be submitted (1984)

Mercury ($^3\text{P}_2$) and ($^3\text{P}_0$) metastable atoms were prepared in a flowing after-glow reactor by flowing He, Ne or Ar carrier gas containing Hg through a hollow-cathode discharge. The interaction of $\text{Hg}(^3\text{P}_2)$ with 30 halogen containing molecules was studied by observation of $\text{HgX}(\text{B})$, $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ emission; the intramultiplet relaxation to $\text{Hg}(^3\text{P}_1)$ also was monitored for some of the molecules, 5 diatomic molecules, NH_3 , CH_4 , and CF_4 . By the addition of N_2 after the discharge, the $\text{Hg}(^3\text{P}_2)$ state can be removed and the reactions of $\text{Hg}(^3\text{P}_0)$ can be studied. The branching fraction for $\text{HgX}(\text{B})$ formation is much lower for $\text{Hg}(^3\text{P}_0)$ reactions than for $\text{Hg}(^3\text{P}_2)$ reactions. The $\text{HgX}(\text{B})$ emission spectra was obtained at sufficiently low pressure that vibrational relaxation is avoided and computer simulation of the spectra gives initial $\text{Hg}(\text{B})$ vibrational state distributions. A close similarity is found for the $\text{HgX}(\text{B})$ branching fractions and vibrational distributions with the analogous $\text{Xe}(^3\text{P}_2)$ atom reactions yielding $\text{XeCl}(\text{B}, \text{C})$ for halogens, mixed halogens, and ICN . The excitation transfer reaction between the $\text{Hg}(^3\text{P}_0, 2)$ and CN also was observed. Upper limits are set for the bond energies of several nitrogen halides ($\text{CF}_3\text{NCl}-\text{Cl}$, $\text{CF}_3\text{NCl}-\text{Br}$, $\text{CF}_2\text{ClNCl}-\text{Cl}$, $\text{CF}_2\text{ClNF}-\text{Cl}$, $\text{CF}_2\text{N}-\text{Cl}$).

5) VIBRATIONAL RELAXATION OF $\text{HgCl}(\text{B})$ AND $\text{HgBr}(\text{B})$ IN Ar AND Ne

Fu Min Zhang, D. Oba and D. W. Setser, J. Phys. Chem., to be submitted (1984)

A hollow-cathode, flowing afterglow apparatus was used to study the vibrational relaxation of $\text{HgCl}(\text{B})$ and $\text{HgBr}(\text{B})$ in a very high vibrational level with Ar and Ne bath gases. The bound-free emission spectra resulting from the reaction of $\text{Hg}(^3\text{P}_2)$ with various chlorine and bromine donors were recorded for 2-20 torr of Ar and Ne. These spectra were simulated to obtain $\text{HgCl}(\text{B})$ and $\text{HgBr}(\text{B})$ vibrational distributions vs. pressure. By using different Cl and Br donors, different ranges of vibrational energy were emphasized. An exponential gap model was used to characterize the V-T energy transfer from each collision. The collision cross-sections are large and near gas kinetic in magnitude. These results are qualitatively similar to those for vibrational relaxation of $\text{XeCl}(\text{B})$ by Ne and Ar.

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